FUEL SYNTHESIS OF SYNGAS USING HYDROTALCITE DERIVED CATALYST

by

Kanagesh A/L Manoharan

14989

Dissertation submitted in partial fulfillment

of the requirements forthe

Bachelor ofEngineering (Hons) (Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

_____

(Dr. BAWADI B ABDULLAH)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

JANUARY 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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KANAGESH A/L MANOHARAN

ABSTRACT

This project investigates the fuel synthesis from syngas using hydrotalcite derived catalyst. The focus of this research is syngas conversion into methanol as an alternative source of fuel. Hydrotalcite derived catalyst was used as it is flexible to reform its structure and have been demonstrated its best performances as catalyst. The range of hydrotalcite derived catalyst will be prepared via co-precipitation method with the aid of metal precursors of nickel, zinc with alumina as support. Hydrotalcite derived catalyst of Ni-Al, Zn-Al and Ni-Zn-Al will be tested throughout this study. The physicochemical and catalytic properties of catalysts was studied usingRAMAN Spectroscopy method, Brunauer-Emmett-Teller (BET) method and Field Emission Scanning Electron Microscopy (FESEM). Catalytic performance of synthesized catalyst was tested using a hydrocarbon cracking reactor to synthesize syngas into methanol. The desired temperature and pressure for this project was fixed at 200℃ and 2 bar respectively. From the overall catalytic reaction, it proves that Zn-Ni-Al has the highest yield of methanol production compared to 2 other bimetallic catalysts. Thecomposition of feed gas used was $CO/H_2/N_2$used was 35/45/20.

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CHAPTER 1 INTRODUCTION

This chapter discusses about the background of study for the final year project. Besides that, this chapter also defines the problem statement, the objective and the scope of the research work.

1.1 Background

In the past years,the tendency to depend on **c**rude oil is as a source for the manufacture of gasoline and fuel synthesis is very high. Subsequently, at this moment, fuel synthesis from biomass and syngas are very much likely to be the alternative technology. Among the popular synthesis of syngas is into higher level alcohol that will be used either in industrial applications or as feed stock for various reactions.

Nowadays, methanol appears to be one of the most promising alternative energy vectors and clean fuel. The methanol production is also highly exothermic. This process will be much faster and higher conversion rate with the presence of catalyst.

For this, hydrotalcite derived catalyst has been considered to improve the fuel synthesis of syngas into methanol. The catalyst samples were prepared by the co-precipitation method. In this research, physio-chemical characteristics and morphologies of the catalysts will be investigated by using Brunauer-Emmett-Teller (BET) method, RAMAN Spectroscopy and Field Emission Scanning Electron Microscopy (FESEM).

1.2 Problemstatement

Although methanol production from syngas is an attractive alternative for producing clean energy fuel, it requires high temperature and pressure reaction. In other words, non-catalytic decomposition of methane can only happen at extremely pressure to obtain reasonable yield of methanol due to the strong C-H bonding within methane. However, the use of hydrotalcite derived catalyst can help to reduce the operation temperatures of thehydrocarbon cracking process and can increase the rate of methanol conversion from syngas. This justifies the need for the development

of a novel catalyst which can enhance methanol production from syngas and have long-term catalyst stability. In addition, it is also important to perform comprehensive study on the catalysis mechanism and catalytic activity which is significant to synthesize a novel catalyst for syngas conversion into methanol.

1.3 Objective

Theobjectives of this project are:

1. To synthesize and characterize hydrotalcite derived catalyst for syngas fuel synthesis.
2. To test the conversion rate of syngas into alcohol focusing on methanol by using hydrotalcite derived catalyst.

1.4 Scope of study

In this final year project, it is hoped to develop three types of hydrotalcite catalyst, which will have metal elements as precursors that will be investigated in the synthesis of syngas for the conversion into methanol. The physio-chemical characteristics and morphologies of the catalysts will be investigated by using RAMAN Spectroscopy, BET and FESEM.

The performance of these three different types of catalyst will be investigated by conducting a laboratory scale experiment in a fabricated reactor for methanol production. The catalytic activity of the catalysts will be evaluated to select the catalyst which will be the most effective and efficient for the production of methanol and the catalyst's mechanism can be further studied.

CHAPTER 2 LITERATURE REVIEW

This chapter discusses about the literature review on the overall project based on previous research on this study. This will discuss the fossil fuel depletion issue, fuel synthesis from syngas, methanol production and also hydrotalcite derived catalyst by relating it to the recentness of past study to improvise this overall project.

2.1Fossil fuel depletion

In the past 15 years,the world has been facing a constant hike in the depletion of fuel source especially in terms of crude oil supply. Crude oil has been the main source for world's most vital traded commodity, supplying fuel for transportation, power generation industry, industrial fuel and lubricants(Utama, Fathoni, Kristianto, & McLellan, 2014).

Various factors have been the influence for the current state of this worrying circumstance. Among those are demand exceeds supply and reduced in production. Demand exceed supply scenario takes place when the number of industrial application and public usage of natural fuel very much higher in terms of value compared to the production rate as the globalization era depends highly on fuel to run(Yusuf et al., 2014). Reduced in production is another main factor contributing in the depletion of fuel resources when it is determined the combustion of fossil fuels tend to produce high quantity of Green House Gasses (Frost, Bahfenne, Graham, & Martens, 2008). From the environmental perspect, it is a very much unhealthy situation as 65% of Green House Gasses contributes to the global warming of the world.

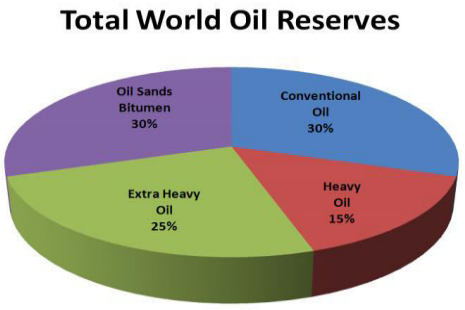


Figure 1: Usage of Oil Reserves According to Industry in Year 2014

Subsequently, the increase in demand of fuel subsequently with the declining rate of oil reserves, tends to be a pulling factor for the research of alternative fuel source (Andersson, Boutonnet, & Järås, 2013). Hence, the chemical industry has made a paradigm shift to research for alternative sources such as natural gas, coal and biomass.

2.2Fuel synthesis from syngas

Syngas basically is a fuel based gas mixture containing mainly hydrogen, carbon monoxide and carbon dioxide (Stelmachowski & Nowicki, 2003). It is also known as synthesis gas. It has been a very much in target for syngas to be synthesized as it can be easily obtained from biomass, coal, and natural gas by gasification method(Liu, Murata, Inaba, Takahara, & Okabe, 2013).

Fuel synthesized from syngas also can be used in various industry of chemicals and engineering as a whole (Dagle et al., 2014).Among those are alcohols based fuel blend have been proven in lowering the amount of pollutant emission. Besides that, finding an effective way in producing high level alcohol is always a challenge which includes equal amount of interest(Mohanty et al., 2014)

2.3 Methanol production

Past years the production of methanol where the raw material is usually generated from the source of coal gasification or natural gas (Li, Hong, Jin, & Cai, 2010). Usage of non-renewable raw material as source of methanol production brings concerns such as pollution to the environment, energy in crisis and depletion of natural resource. The CAMERE (carbon dioxide hydrogenation to methanol via reverse water gas shift) process, steam reforming, liquid phase methanol process, and synthesis from syngas are among the methods of methanol production (Anicic, Trop, & Goricanec, 2014).

The synthesis of syngas process route in methanol production is a very much common and commercially used in the petrochemical industry. This method has been initiated in the late 1970's where it had successfully derived methanol from syngas with much draw back as part of the process (Mao, Yang, Xia, Zhang, & Lu,

2006).

Among the problems faced for syngas synthesis is the force to produce cleaner fuels and chemicals with directly less amount of sulphur. Besides that, high efficiency of syngas conversion only occurs at high pressure. Moreover, the catalytic conversion of syngas process is also very much endothermic where it requires high temperature.

The main methanol synthesis reaction may be written:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -91\ kJ/mol$$

Equation 1: Methanol Synthesis

Based on the energetics of the reactions, to stimulate a high yield of methanol production needs high pressure and high temperature(Dagle et al., 2014)

Usually the syngas which would be obtained from a specific gassifier will be further used for the methanol production. Due to the insufficient level of hyrdrogen, water gas shift reaction would be undergone by the syngas before being sent to the methanol synthesis specified reactor. Besides that, syngas conversion does not take place in the absence of catalyst as they are the factor influencing the production of yield, reducing the side reactions and enhancing the activation energy for a shorter time process (van Bennekom, Venderbosch, Assink, Lemmens, & Heeres, 2012).

This research will be focusing on the production of methanol from the syngas with the presence of hyrdotalcite catalyst in order choose the optimum catalyst in terms of performance rate with the aid of hydrocarbon cracking reactor.

2.4Hydrotalcite derived catalyst

Researchers have reported that the rate of methanol production activity with aid of catalyst by transition metals follows the order: Co, Ru, Ni, Rh> PT, Re, Ir> Pd, Cu, W, Fe, Mo (Siew et al., 2015). The presence of catalysts provides an alternative reaction mechanism involving a different transition state and lower activation energy. Hence, more molecular collisions have the energy required to reach the transition state and enable the reaction to take place at lower temperature as indicated in Figure 2.

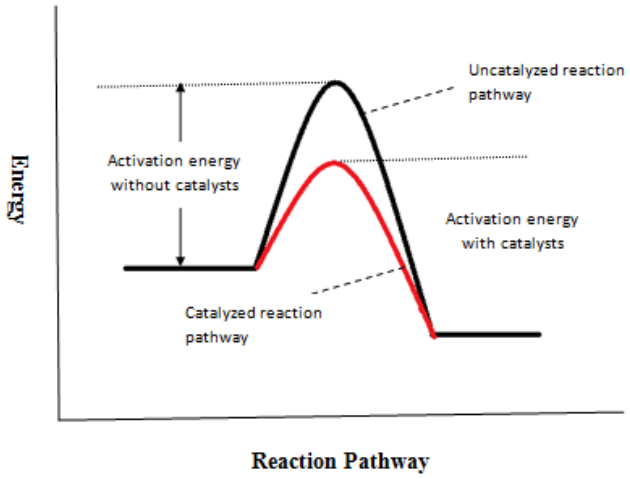


Figure 2: Potential energy diagram showing the effect of a catalyst in chemical reaction

In the very recent years, the tendency and attention received for the usage of hydrotalcite like compounds (HTLCs) as catalyst is very high. This is mainly supported by the unique properties of these catalyst exhibit(Zhao, Yi, Tang, & Song, 2013). It was also mentioned that there are high possibilities for HTLCs to lose crystal water. Another positive impact which was added in their research was that HTLCs will always exhibit good activity and performance rate which is supported because of its large surface area, basic properties and also high metal dispersion.

Hydrotalcite compound based catalysts usually tend to be a layered material. It also usually been formed when the positively charged layers of edge sharing tend to be substituted by $Mg(OH)_6$octahedra(Basile, Benito, Fornasari, & Vaccari, 2010). Basically the main general formula of Hydrotalcite compound is said to $[M^{2+}{}_{1-}{}_XM3+{}_X(OH)_{2]($A^{n-}{}_{x/n)n}H_2O$(Cantrell, Gillie, Lee, & Wilson, 2005).

Table 1: Recent study oncatalyst preparation and production of methanol from syngas

Num	Type of Catalyst	Catalyst Preparation Technique	Major Findings	References
1.	K–Ni–MoS_2	Co-Precipitation	• The long-term change which was going on during the whole experiment with continuously increasing catalyst activity as well as decreasing alcohol and increasing hydrocarbon selectivities. • A remarkable transformation	(Andersson et al., 2013)

			was seen for the K_2CO_3-promoted MoS_2 catalyst after storage in air for a couple of weeks, which led to a shift from being an alcohol promoter when fresh to becoming a hydrocarbon chain-growth promoter	
2.	Cu/Fe/Mn/Zn	Co-Precipitation	• A series of Cu/Fe/Mn/Zn catalysts developed group showed > 50% total alcohol selectivity and > 50% C2+OH selectivity.	(Xiao et al., 2013)
3.	Zn–Al hydrotalcite catalyst	Co-Precipitation	• The results showed that the Zn–Al hydrotalcite-like compounds were efficient precursor in preparing active and stable catalysts for alcohol conversion and hydrolysis of COS.	(Zhao et al., 2013)
4.	Acetogens Microalgae	Microalgae precipitation	• Microalgae catalyst shows conversion of ethanol and higher alcohols but in a lowered scaled.	(Gao, Atiyeh, Phillips, Wilkins, & Huhnke, 2013)
5.	Fe/Co/Mo/Ni/c-Al_2O_3	Incipient wetness Impregnation	• Only Fe, Co, Ni and Ru metals have sufficiently high activities for the FTS process. • Among these four metals, only cobalt and iron-based catalysts can be considered as practical catalysts for kerosene and alcohol conversions.	(Yan et al., 2013)
6.	Pd/ZnO/Al_2O_3	Incipient wetness impregnation	• The Pd/Zn/Al_2O_3 catalyst was found to be highly stable and resistant to sintering under the conditions of the testing, in contrast to the industry standard Cu/ZnO/Al_2O_3 methanol catalyst in hydrocarbon production.	(Dagle et al., 2014)
7.	Cu:Zn	Co-Precipitation	• The reaction results showed that the conversion of Cu0.4–Zn0.6–O catalyst to DME was higher than that of Cu–Zn–O catalyst. • All in all,both the preparation method and the molar ratio of Cu–Zn are responsible for the catalytic activity of the prepared catalysts for higher alcohol conversion.	(Wang et al., 2013)
8.	MoS_2/Zn	Incipient	• The catalyst performance is	(Ferrari et al.,

		wetness impregnation	strongly affected by the alkali addition method. The addition of potassium by physical mixing (MoS_2/Zn PM 6 K_2CO_3) yields higher selectivity to ethanol while the methanol selectivity follows the same trend as for the impregnated samples.	2013)
9.	K-promoted Cu-Zn-Al catalysts	Co-Precipitation	• The main reaction products over the K-promoted Cu-Zn-Al catalysts were alcohols, with methanol being the major carbon oxygenated product, along with CO_2 and small concentrations of hydrocarbons.	(Heracleous, Liakakou, Lappas, & Lemonidou, 2013)
10	Cu/ZnO	Co-Precipitation	• Temperature for methanol production was set at 250℃ and at 8 bar of pressure. • Cu/ZnO 8 catalyst prepared at pH 8 showed the best catalytic performance due to the finely dispersed Cu particles and the high strong acidity. • In addition, the catalytic activity of Cu/ZnO 8 catalyst maintained at the same level even after a 60 h-catalytic reaction, leading to the high feasibility of application of Cu/ZnO 8 catalyst to the continuous reaction system alongwith the batch reaction system for methanol production from syngas.	(Jeong et al., 2015)
11	Cu/ZnO/Al_2O_3	Incipient wetness impregnation	• The catalytic performance of bimetallic catalyst is considered better than monometallic catalyst and therefore, it has attracted the research attention for further development. • The purpose of introducing metal/metal compound to the catalyst is to better tune the selectivity and to enhance the activity of the catalyst	(Ali, Abdullah, & Mohamed, 2015)
12	Hybrid catalyst Cu-ZnO and Pd/ZSM-5	Impregnation method	• Hydrocarbon yield was drastically increased by co-feedingn-hexane with syngas to the catalyst, and increased from ca. 29%to ca. 54% with the increase in the partial pressure of n-hexanefrom 0 to 1.5 MPa.	(Ma et al., 2014)

			• ZnO showed better catalytic activity compared to Cu	
13	Cu/CeO_2 and $Cu/ZnO/Al_2O_3$ /Rh/C, Rh/H-MOR and Cu/SiO_2	Co-Precipitation and Impregnation method	• Effective $Rh/Cs_2H_2SiW12O40$ catalyst for the DME carbonylation but a high CO/DME ratio was still needed to improve the DME conversion. • Cu/CeO2 showed a high catalytic performance for the methyl acetate hydrogenolysis because both Cu0 and Cu+ species could be stabilized in the Cu/CeO2 catalyst.	(Liu, Murata, Inaba, & Takahara, 2013)
14	$Cu/ZnO/Al_2O_3$	Two-step precipitation method	• It can be seen that, before the ATD test, the CO conversion (60.7%) over blank CZA catalyst was quite lower than that (65.9%) over CX catalyst. • However, as the introduction of the surfactant in preparing the binary matrix, the CO conversion over resultant CZA catalysts increased significantly and was higher than that over CX catalyst, in which CO conversion reached 71.1% over both 5P-CZA and 10T-CZA	(Chu, Chen, Yu, Wang, & Fang, 2013)
15	Zr-doped $Ni/c\text{-}Al_2O_3$	Impregnation co-precipitation (ICP) method	• The larger amount of reducible Ni formed using the ICP method gave a better catalytic performance.	(Zhang et al., 2014)

2.5 Selection of transition metal for methanol production from syngas

Based on the critical analysis on the literature review, Nickel (Ni) and Zinc (Zn) have been chosen as the respective transition metal for catalyst development in methanol production from synthesis gas. This is very much supported by the previous research done stating that Ni catalyst are reasonably effective in syngas conversion to higher alcohols at 250℃ and above (Zhang et al., 2014) . Hence for this project, Ni catalyst will be tried in a lower temperature at 200℃to check on its catalytic reaction level. There are certain limitations for Ni catalyst where they need a good support and tend to sinter early if they are any deposition in the surface area.

Moreover, Zinc (Zn) is selected as it has been very much technically proven that Zn plays a major significant role where it can significantly produce methanol at a higher temperature

(>350℃) (Chu et al., 2013). This study will be good to further improve and validate that Zn catalyst can be generous in methanol production even at a lower temperature. Therefore, the present study is aimed to investigate the improved activity of alumina supported Ni catalysts and Zn catalyst at a lower temperature and pressure.

In addition, this study will also study the trimetallic combination of Ni and Zn with the support of alumina in production of methanol production. This study on this combination is very much limited as it is a rear combination and methanol production prefers high temperature and pressure condition for a reasonable yield.

CHAPTER 3 METHODOLOGY

This chapter discusses about the research methodology and project activities that are planned for the project. Besides that, this chapter also includes the discussion about the raw materials and chemicals that are required, the synthesis method of the catalyst, the technique which will be employed to characterize the catalysts, the technique to evaluate the performance of the catalysts. The key milestone and gantt chart is also attached along in this chapter.

3.1 Research methodology

The planned project activities for this research are fully experimental work based. Once the literature review is completed, experimental work can be conducted to develop the hydrotalcite derived catalysts which will be tested to evaluate their efficiency in conversion of syngas into methanol. Figure below demonstrates the flow of the research work in this study.

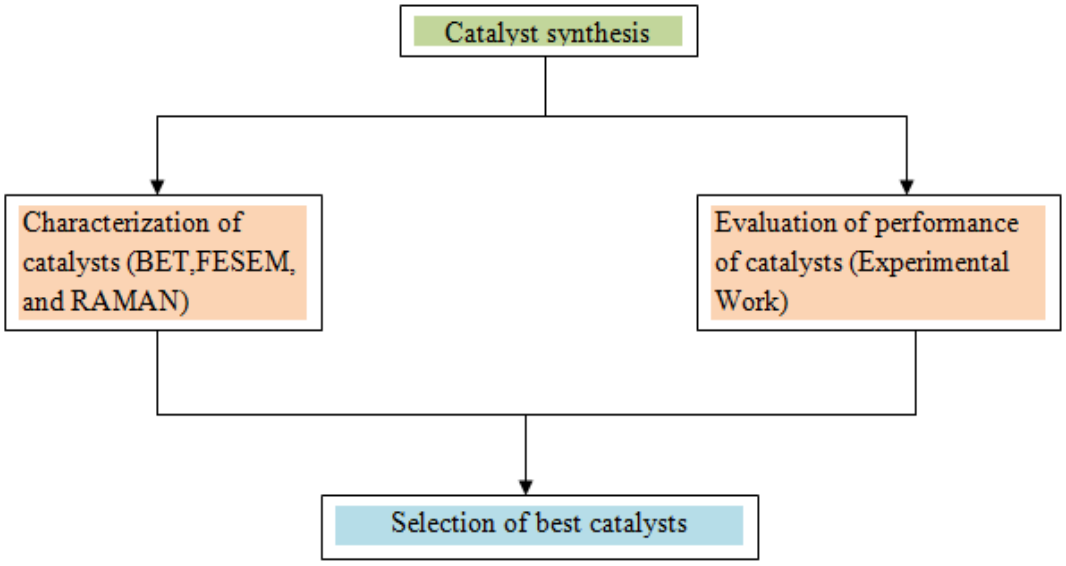
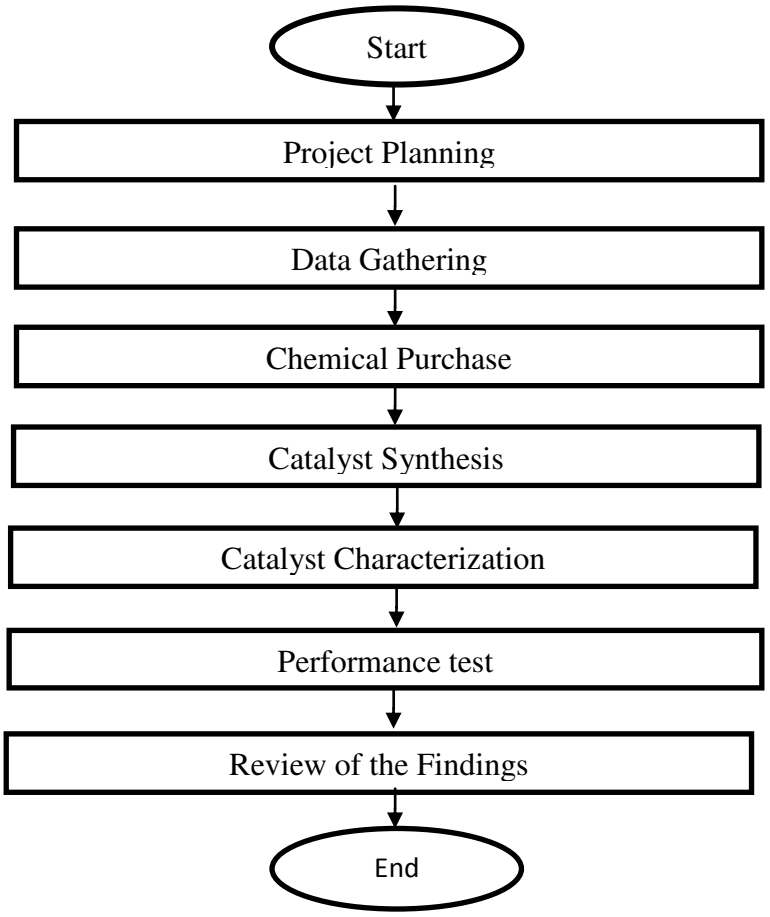


Figure 3: Basic Guide on Overall Project



Project Workflow

3.2 Raw materials and chemicals needed

In this research work, several raw materials and chemicals are required to ensure the success of the project. They are listed as follows:

i) Laboratory-scale pure gases:
Syngas(H_2,CO) and Inert Gas (N_2)

ii) Chemicals
Sodium carbonate decahydrate $Na(CO_3)_2$, aluminium nitrate nonahydrare $Al_2(NO_3)_3.9H_20$, nickel (II) nitrate hexaydrate $Ni(NO_3)_2.6H_20$, and zinc nitrate hexahydrate $(Zn(NO_3)_2).6H_20$

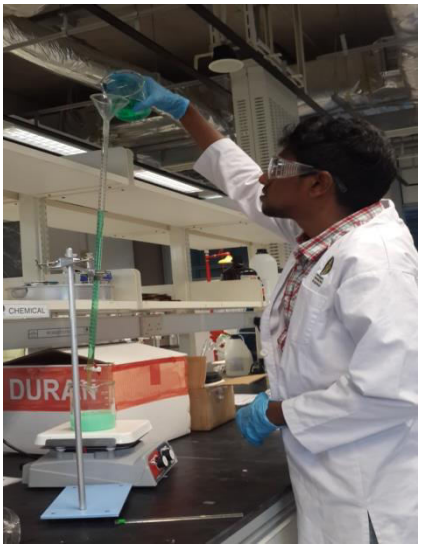
3.3 Catalyst synthesis

Three catalyst samples of Ni-Al, Zn-Al and Zn-Ni-Al of molar ratio 3:1, 3:1 and 2:1:1 were prepared respectively via co-precipitation method. Ni and Zn acts as the metal precursors while aluminium nitrate nonahydrate (Al) acts as the support for the catalyst. Sodium carbonate decahydrate ($Na_2CO_3.10H_2O$) acts as the precipitating agent for the respective samples. The preparation for co-precipitation synthesis was started by preparing solution of

metal precursors, support and also precipitating agent. Metal precursors solution is then mixed with support solution before being titrated into the sodium carbonate decahydrate solution. Constant stirring at 55°C was achieved throughout the titration process with the aid of magnetic stirrer and hot plate. Once the precipitate formed, it was then filtered using filter paper. Subsequently, the filtered samples were dried in the oven for 12 hours at 110°C in order to produce dried hydrotalcite derived catalyst. Mixed oxide conversion of the hydrotalcite derived catalyst was achieved via calcinations at 500°C for 6 hours.

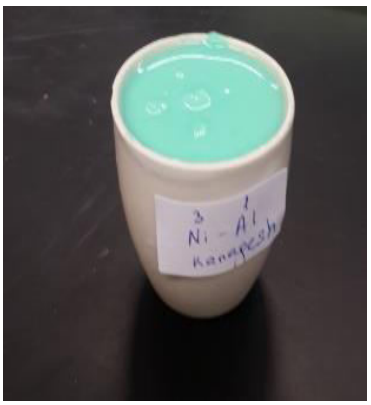
Catalyst Preparation Workflow

Titration of Metal Precursors Solution into the Sodium Carbonate Decahydrate Solution



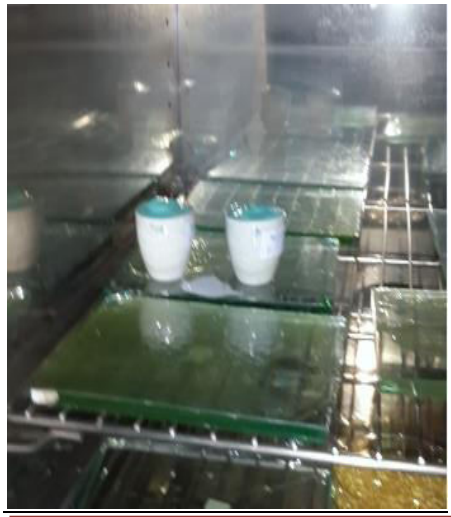
Addition of Metal Precursors Solution into the burette

Filtration of the sample and collecting the precipitate



Sample after filtered

Catalyst Preparation Workflow(Continued)



Placement of filtered sample into the oven at 110℃

Dried fresh hydroltacite derived catalyst

Calcined catalyst(mixed oxide) stored in a vial

Calcination of catalyst at 500℃

3.4 Characterization of catalysts

The following analysis is planned to be conducted for the characterization of the catalysts.

i) RAMAN Spectroscopy Analysis

RAMAN Spectroscopy Analysis provided detailed information on the molecular vibrations on the respective of the samples of the catalyst. It provided thorough identification and quantization of the specified catalyst sample.

ii) Brunauer-Emmet-Teller (BET) Surface Area Analysis

The BET Surface Area Analysis aimed to provide precise specific surface area evaluation of the catalysts by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. This technique encompasses external area and pore area evaluations to determine the total specific surface area to study the effects of surface porosity and particle size in influencing methanol conversion from syngas.

iii) Field Emission Scanning Electron Microscopy (FESEM) Analysis

FESEM provided topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth of field.

3.5 Evaluation of catalyst performance

All the catalyst will be tested with the syngas presence in a hydrocarbon cracking tubular reactor for the conversion into methanol. The time taken, temperature, pressure and other operating condition will be manipulated accordingly to choose the best catalyst for the conversion of syngas into methanol. The process and procedure are summed up below:

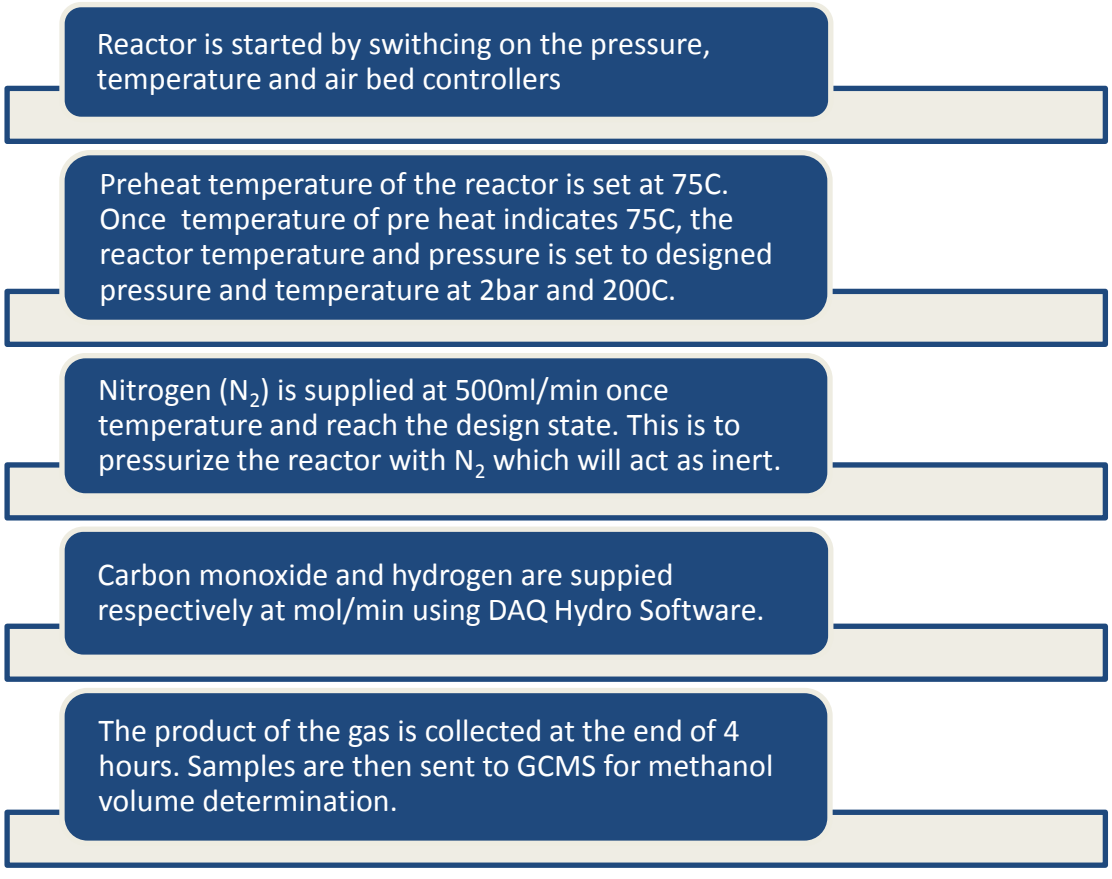


Figure 4: Reactor Start Up Procedure

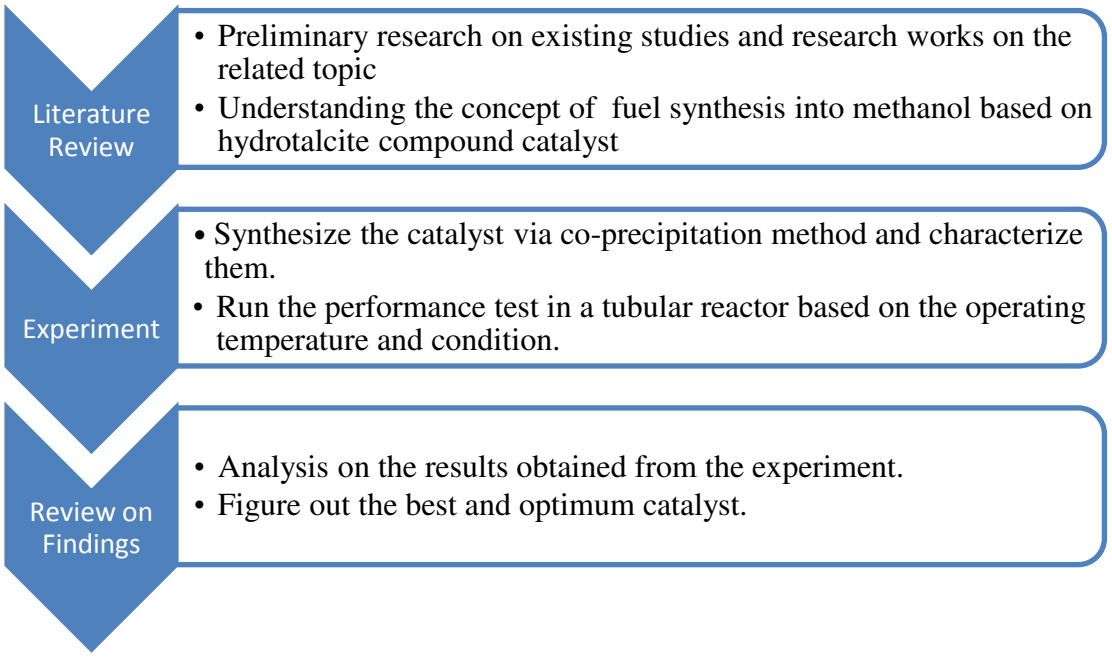
Catalyst Performance Evaluation Workflow

Catalyst placed in the reactor tube is adjusted for the best position

Reactor tube is placed back in the reactor and they are tightly closed.

Product is then collected in air bag after 4 hours of experiment duration.

3.6 Key milestone



3.7 GanttChart

FYP 1

No	Detail	Weeks													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Title and Supervisor Allocation		■												
2	Preliminary Research Work		■	■	■										
3	Preparing Extended Proposal				■	■	■								
4	Submission of Extended Proposal						■								
5	Proposal Defense								■						
6	Project Work Continues						■	■	■	■	■	■	■	■	■
7	Submission ofInterim Draft Report												■		
8	Submission ofFinal InterimReport														■

Figure 5: FYP1 gantt chart

FYP 2

No	Detail	Weeks													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Catalyst Sample Preparation		■	■											
2	Catalyst Characterization				■	■	■	■	■	■	■				
3	Methanol Production								■	■					
4	Testing of Sample (Methanol Content)										■				
5	Submission of Progress Report								■						
6	Project Write Up						■	■	■	■	■	■	■	■	■
7	Submission ofDissertation														■

Figure 6: FYP II gantt chart

CHAPTER 4 RESULTS AND DISCUSSIONS

This chapter discusses about the results obtained and its respective discussion by referring to the experimental work that have been done so far. The results can be divided into 3 main parts which are the catalyst sample preparation, catalyst characterization and finally the performance of catalyst in the production of methanol.

4.1 Catalyst preparation

This part discusses the catalyst preparation methods beginning from the samples calculation method for co-precipitation synthesis till the hydrotalcite derived catalyst and mixed oxide is formed.

Table 2: Used chemical and their molecular weights

Chemical Name	Symbol	Molecular Weight (g/mol)
$Ni(NO_3)_2.6H2O$	Ni	290.810
$Zn(NO_3)_2 \cdot 6H2O$	Zn	297.470
$Al(NO_3)_3.9H2O$	Al	375.120
$Na_2(CO3)_2.10H2O$	Na	286.12

The calculation which have been used is based on the 25gm of total weight of the catalyst sample $Ni(NO_3)_2.6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ with their respective support of $Al(NO_3)_3.9H2O$ and precipitating agent $Na_2(CO_3)_2.10H2O$.

Table 3:Weight of chemicals used based on the molar ratio

Molar Ratios	Nickel (Ni)	Zinc (Zn)	Aluminium (Al)
Ni : Al = 3:1	19.8662g	-	5.1338g
Zn : Al = 3: 1	-	19.7732g	5.2268g
Zn:Ni:Al = 2:1:1	5.8903g	11.5171g	7.5926g

Sample calculation for the weight of chemicals based on the molar ratios is done below for the sample Ni: Al = 3:1.

Combination Ni : Al = 3:1.

X + Y = 25g ------- (Equation 1)

$$\frac{X}{MolecularWeightX} + \frac{Y}{MolecularWeightY} = 25g$$

$$\frac{X}{290.810} + \frac{Y}{375.12} = 3:1$$

$$\frac{X}{Y} + \frac{375.12}{290.810} = 3:1$$

$$\frac{X}{Y} = 3\ (1.2899)$$

X = 3.8697 Y------- (Equation 2)

Substitute Equation 2 into Equation 1

3.8697 Y + Y = 25g

4.8697 Y = 25g

Y = 5.1338 g

X= 25g – 5.1338g

X = 19.8662g

Hence the combination metal of Ni : Al (3:1) uses respectively 19.8662g of Ni and 5.1338 g of Al. Respective other combination of metals did use the same the calculation steps to determine the weight of the chemicals needed for the co-precipitation method.

Next is the calculation of required of total amount of $Na_2(CO_3)_2.10H2O$ for each catalyst sample. The formula used is as below:

$W_T = W_1 + W_2 + W_3$

The respective variables are

W_1= Required amount of $Na_2(CO3)_2.10H2O$ for Ni precursor

W_2= Required amount of $Na_2(CO3)_2.10H2O$ for Zn precursor

W_3= Required amount of $Na_2(CO3)_2.10H2O$ for Al precursor

Therefore,

$W_T =$

$$1.1X\left[\left(\frac{Weight\ of\ Ni}{MW}\right) + \left(\frac{Weight\ of\ Zn}{MW}\right) + \left(\frac{Weight\ of\ Al}{MW} X \frac{2}{3}\right)\right] X\ MW\ of\ W$$

Table 4: Molar ratio and required amount of sodium carbonate decahydrate

Molar Ratio	Required amount of $Na_2(CO3)_2.10H2O$ with extra 10wt%
Ni : Al = 3:1	24.3677g
Zn : Al = 3: 1	23.8531g
Zn:Ni:Al= 2:1:1	22.8052g

Sample calculation for the required amount of required amount of $Na_2(CO_3)_2.10H_2O$ based on the molar ratios is done below for the sample Ni : Al = 3:1.

$W_T = W_1 + W_2$

$$W_T = 1.1X\left[\left(\frac{Weight\ of\ Ni}{MW}\right) + \left(\frac{Weight\ of\ Al}{MW} X \frac{2}{3}\right)\right] X\ MW\ of\ W$$

$$= 1.1X\left[\left(\frac{19.8662}{290.810}\right) + \left(\frac{5.1338}{375.120} X \frac{2}{3}\right)\right] X\ 286.12$$

= 24.3677g

4.2 Catalyst Characterization

There are 3 types of catalyst characterization which the respective catalyst sample will pass through. They are RAMAN Spectroscopy, BET, and also FESEM.

4.2.1 RAMAN spectroscopy analysis

RAMAN Spectroscopy plays a major role in determining the appropriate quantification and respective molecular vibration at its excited state of a sample. The highest peaks of the RAMAN Spectroscopy were studied and retrieved to know the level of combination of metals and its molecular vibration (Yang, Kraytsberg, and Ein-Eli (2015)

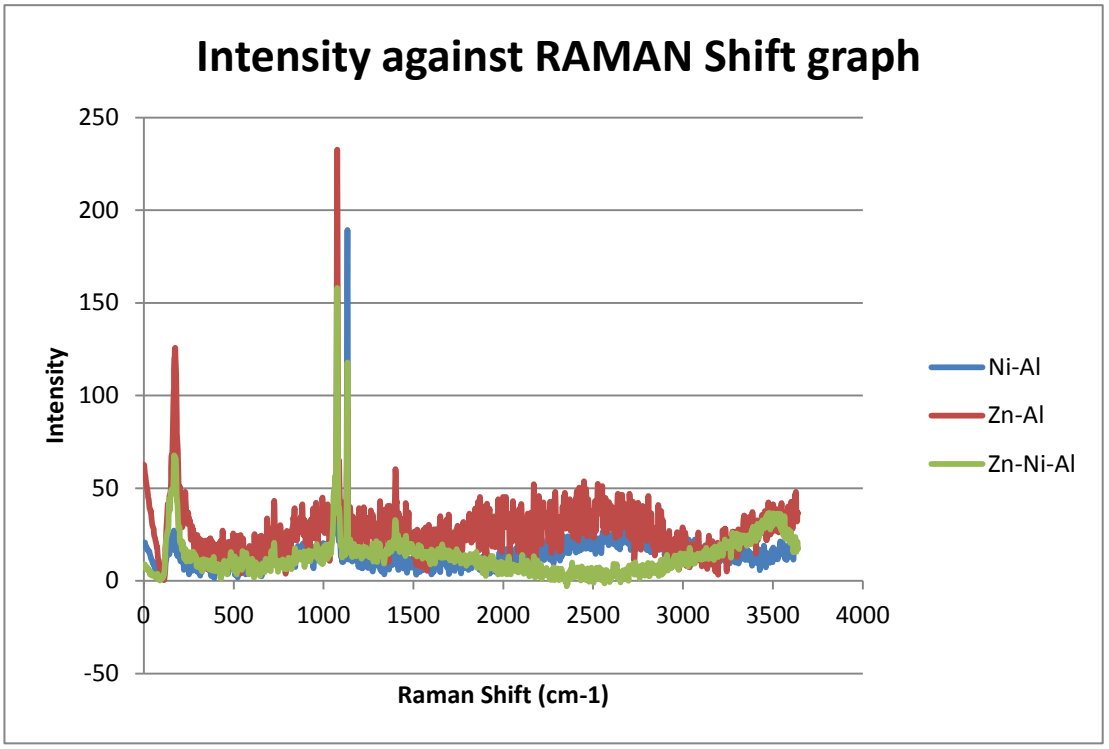


Figure 7: RAMAN Spectroscopy of the catalyst samples

Figure 7 above shows RAMAN Spectroscopy of Ni-Al, Zn-Al and Zn-Ni-Al. Ni-Al is represented with green line, followed by Zn-Al in red line and Zn-Ni-Al in blue colour line. Molecular vibrations of the respective component atom are highest at the each peak(Yang et al., 2015). Besides that it can be deduced that distance of each peak respective of the RAMAN shift shows the molecular size of the atoms present(Dobrea et al., 2015). From Figure 7, the smallest molecular based on the distance of peak referring to RAMAN Shift is Al, followed by Ni and Zn.

4.2.2 Brunauer–Emmett–Teller (BET) Surface Area Analysis

The BET Surface Area Analysis is aimed to provide precise specific surface area evaluation of the catalysts by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. This technique encompasses external area and pore area evaluations to determine the total specific surface area to study the effects of surface porosity and particle size of the respective catalyst in methanol conversion of syngas. The high surface area of adsorbents is desirable as it generally gives high number of adsorption-desorption sites. In order to study the specific surface area and the porosity of the catalyst samples, nitrogen adsorption-desorption related study was conducted. This study was conducted using *Micromeritics ASAP 2020 V3.04 H*.

Table 5: Summary of pore and surface area based on BET analysis

Material	**BET Surface Area (m^2/g)**	**Pore Volume (cm^3/g) [BJH Desorption Cumulative Volume]**	**Pore Size (Å) [BJH Desorption average pore width (4V/A)]**
Ni-Al	21.2502	0.022198 cm³/g	121.647 Å
Zn-Al	16.4342	0.108514 cm³/g	193.1819 Å
Zn-Ni-Al	28.6972	0.186399 cm³/g	102.130 Å

The result observed is in agreement with the findings that with drying at intermediate temperatures without losing the hydrotalcite structure, the surface area and pore volume increases. This is due to the formation of micropores and mesopores in the sample caused by the removal of air and water duringcalcinations process where the process took place without altering the crystal morphology of the samples.

The pore size of the materials was measured through N_2adsorption technique. As can be seen from Table 6, all samples are of mesopore size (20-500Å). The material with the highest pore size is Zn-Al catalyst with molar ratio of 3-1and a pore size of 193.1819Å. The larger the pore size, the smaller the BET

surface area. Hence, this reduces the catalytic reaction which is very much dependent on the surface area, as larger surface area promotes higher range of catalytic reaction to take place at the catalyst sample which will improve the methanol production from synthesis gas. It is because the main platform for reaction to speed up is at the catalyst surface area as this is being supported by the research done by (Anicic et al., 2014).

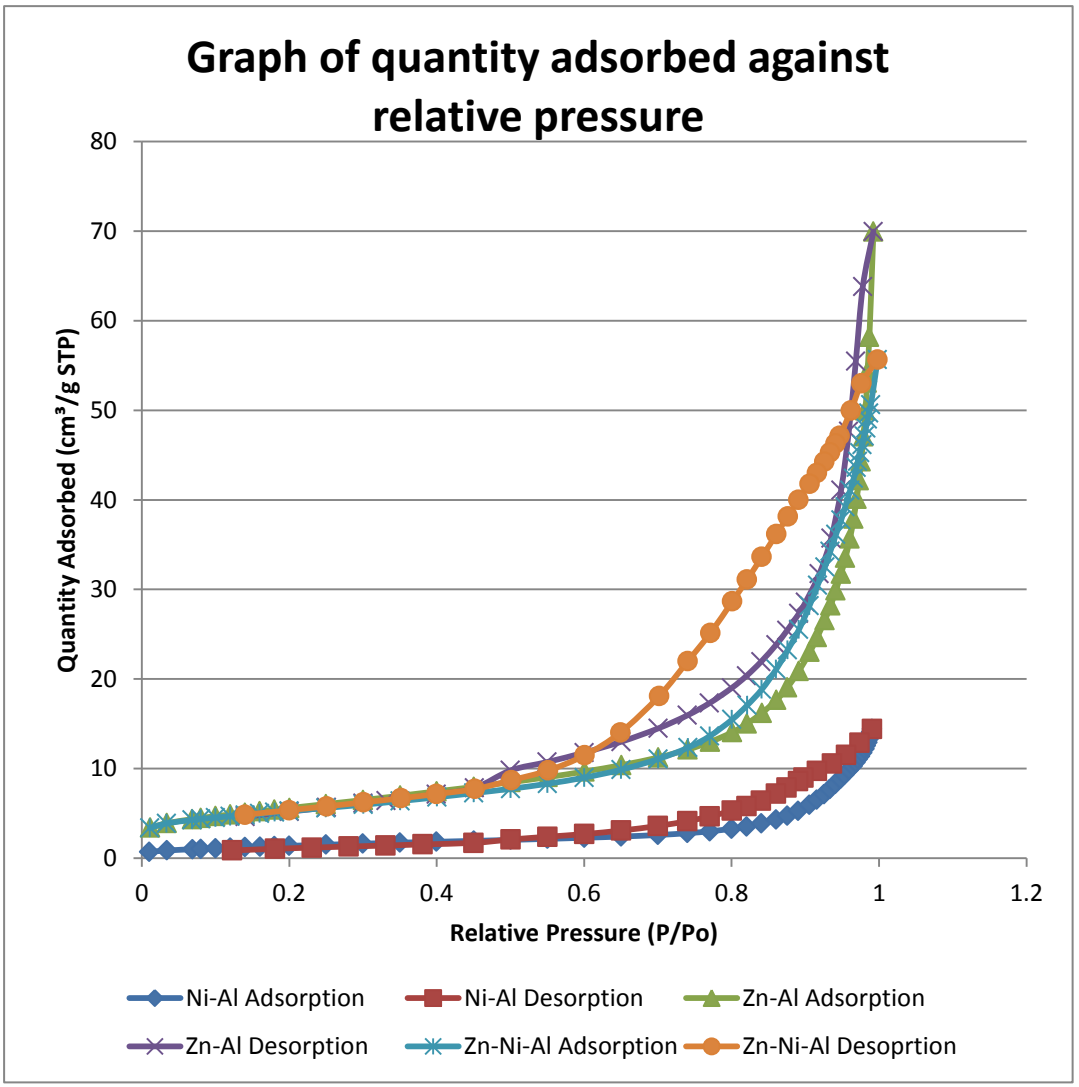


Figure 8: BET adsorption and desorption theorem

Figure above shows the respective results for the BET analysis of the 3 catalyst samples which underwent degassing of nitrogen at 200℃. Based on the tabulated graph, it proves that these catalysts follow Type II and Type III Adsorption Theorem.

Ni-Al Adsorption graph is the only one which follows type II adsorption theorem meanwhile the others follows the Type III adsorption theorem. Both of

these type has a similarity as mentioned by (Ladavos et al., 2012) where the gas-solid adsorption of metal precursor based material or catalyst with meso- to macro-porosity that has a mixture of strong and weak adsorbate-adsorbent interaction.

Type III Adsorption Theorem proves that this isotherm shows very much high deviation from the Langmuir model. Besides that, this type of isotherm explains the formation of multilayer of the reaction. Referring to the graph above, it shows that there is no flat portion in the graph which proved that monolayer formation is not present in the overall reaction. It indicated that the respective catalyst have weak interactions with nitrogen gas.

4.2.3 Field Emission Scanning Electron Miscroscopy (FESEM) Analysis

Field emission scanning electron microscopy was conducted using *Philips XL30/FEI ESEM* operating at an accelerating voltage from 5 to 30kv. The FESEM images were taken at 1x, 5x, and10x magnification. The FESEM images representative of the morphology of the catalysts in their as produced state are indicated below with different magnification as follows.

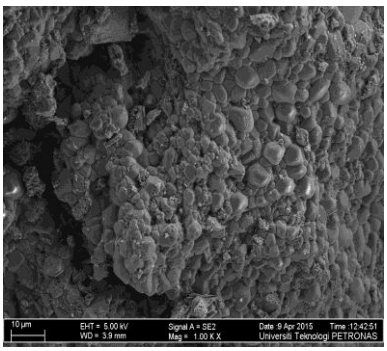


Figure 12: FESEM images of Ni-Al at 1x magnification

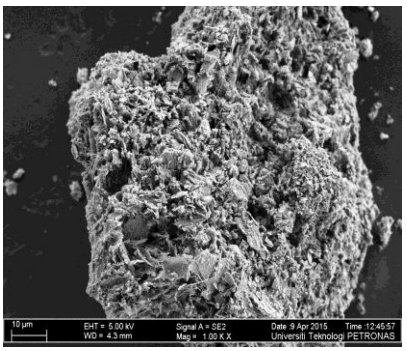


Figure 13: FESEM images of Zn-Al at 1x magnification

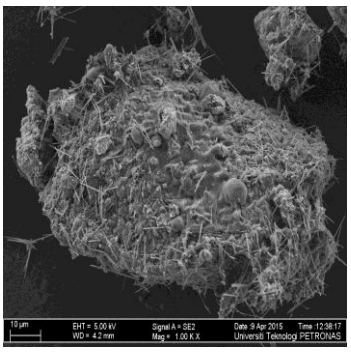


Figure 14: FESEM images of Zn-Ni-Al at 1x magnification

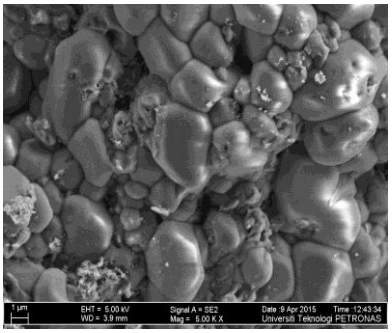


Figure 9: FESEM images of Ni-Al at 5x magnification

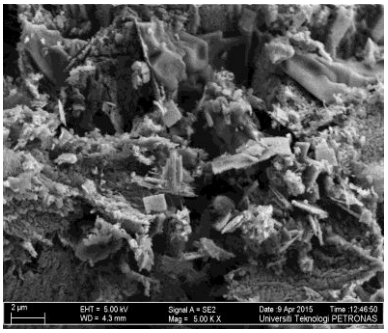


Figure 10: FESEM images of Zn-Al at 5x magnification

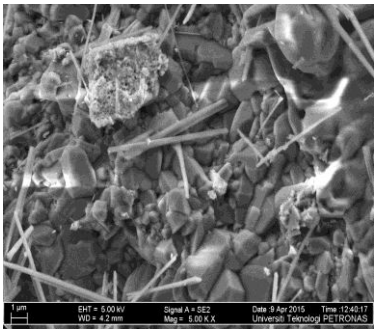


Figure 11: FESEM images of Zn-Ni-Al at 5x magnification

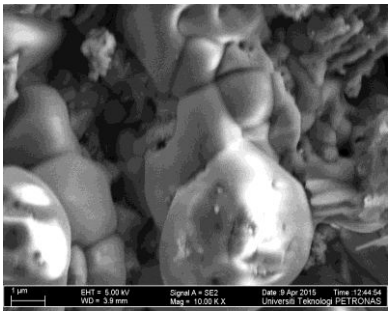


Figure 17: FESEM images of Ni-Al at 10x magnification

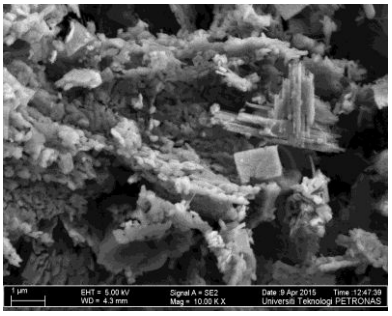


Figure 16: FESEM images of Zn-Al at 10x magnification

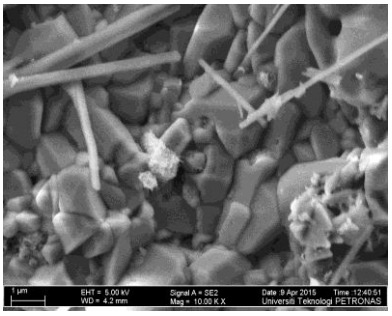


Figure 15: FESEM images of Zn-Ni-Al at 10x magnification

FESEM images above indicate that the Ni-Al catalysts exhibits cubic shape while the Zn-Al catalysts demonstrated thin layer of square surface . Zn-Ni-Al catalyst shows a combination of geometrical structure of both. In addition, it can be observed that smaller nickel and zinc particles were dispersed on the surface of Al_2O_3 support for the Ni-Al, Zn-Al and Zn-Ni-Al catalysts structures. Smaller pore size and larger surface area have been considered as one of the main factors for the development of effective catalysts for methanol production process because large particles dispersion may promote the formation of carbon on the surface of the catalysts hindering metal dispersion, thereby causing deactivation and sintering of the catalysts.

Besides that, Zn-Ni-Al shows a better homogenous morphology comparable to Ni-Al and Zn-Al structure. The trimetallic catalyst structure which shows higher homogenous structure will enable easier dispersion of nickel and zinc metal to speed up the production of methanol and reduce the activation energy.

Moreover, Energy Dispersive X-ray Spectroscopy (EDX) mapping was completed to evaluate the dispersion of nickel and zinc metal particles with Al_2O_3 support which would play a significant role in the catalytic reaction.

4.2.4 Energy Dispersive X-ray Spectroscopy (EDX) Analysis

EDX analysis was performed on a *Philips XL30/FEI ESEM*. The main objective is to determine the actual and uniform nickel and zinc metal dispersion. Besides that, the atomic percentage of the individual elements were determined from

the EDX mapping to evaluate whether correct amount of metal precursors have been incorporated into the synthesized catalysts using the co-precipitation method. Any discrepancies with the theoretical and experimental value would be an improvement platform for the preparation of catalyst in future studies. Results of EDX analysis are tabulated below:

Table 6: Determination of weight and atomic percentage of elements for Ni-Al catalyst

Atomic Number	Element	Weight Percentage (%)	Atomic Percentage (%)
13	Aluminium	15.75	22.12
8	Oxygen	8.98	21.27
28	Nickel	67.26	67.26
11	Sodium	8.01	13.20
Total		100	100

Table 7: Determination of weight and atomic percentage of elements for Zn-Al catalyst

Atomic Number	Element	Weight Percentage (%)	Atomic Percentage (%)
13	Aluminium	16.23	24.80
8	Oxygen	7.02	18.09
30	Zinc	69.26	43.68
11	Sodium	7.49	13.43
Total		100	100

Table 8: Determination of weight and atomic percentage of elements for Zn-Ni-Al catalyst

Atomic Number	Element	Weight Percentage (%)	Atomic Percentage (%)
13	Aluminium	11.01	16.82
8	Oxygen	8.19	21.10
28	Nickel	25.3	17.77
30	Zinc	47.49	29.94
11	Sodium	8.01	14.36
Total		100	100

EDX mapping results tabulated above shows that nickel and zinc have combined respectively in perfect manner based on the molar ratio of the combinations for the catalysts. The uniform and perfect dispersion of the metal precursors may have strengthened the catalyst and thereby enabled effective methanol production process to take place. In addition, the active metals distribution and placement in the sample catalyst in an even manner is expected to contribute towards a successful production of methanol from synthesis gas feed stock. This also supports that trimettalic with even dispersion posses higher catalytic reaction ability to break the bonds of C-H in methane to form methanol.

It is found that in each catalyst samples sodium and oxygen are found in traces amount. Presence of sodium is very much reasonable when sodium carbonate decahydrate was used as precipitating agent for allthe catalyst sample for synthesizing process. Besides that, presence of oxygen in each sample is justified when process of synthesizing took place in a laboratory environment which is at room temperature. Traces of oxygen are only present as it is believed that during drying and calcinations would have removed the excess.

Overall this EDX analysis proves that each catalyst samples are successfully are synthesized by co-precipitation method in the best manner to support the production of methanol process from synthesis gas.

4.3 Methanol production

For this project synthesis gas is in the form CO and H_2 which was purchased directly from Linde. Thecomposition of feed gas was $CO/H_2/N_2$ = 35/45/20, inwhich nitrogen was employed as an internal standard. The reaction temperature and pressure was set at 200℃ and 2 bar respectively which is to further improve the studies from (Jeong et al., 2015) which uses 230℃ and 10 bar range of operating condition. The subsequent product was captured in air bag and sent to Gas Chromatography Mass Spectrometer instrument to determine the composition of respective components. The results are discussed below.

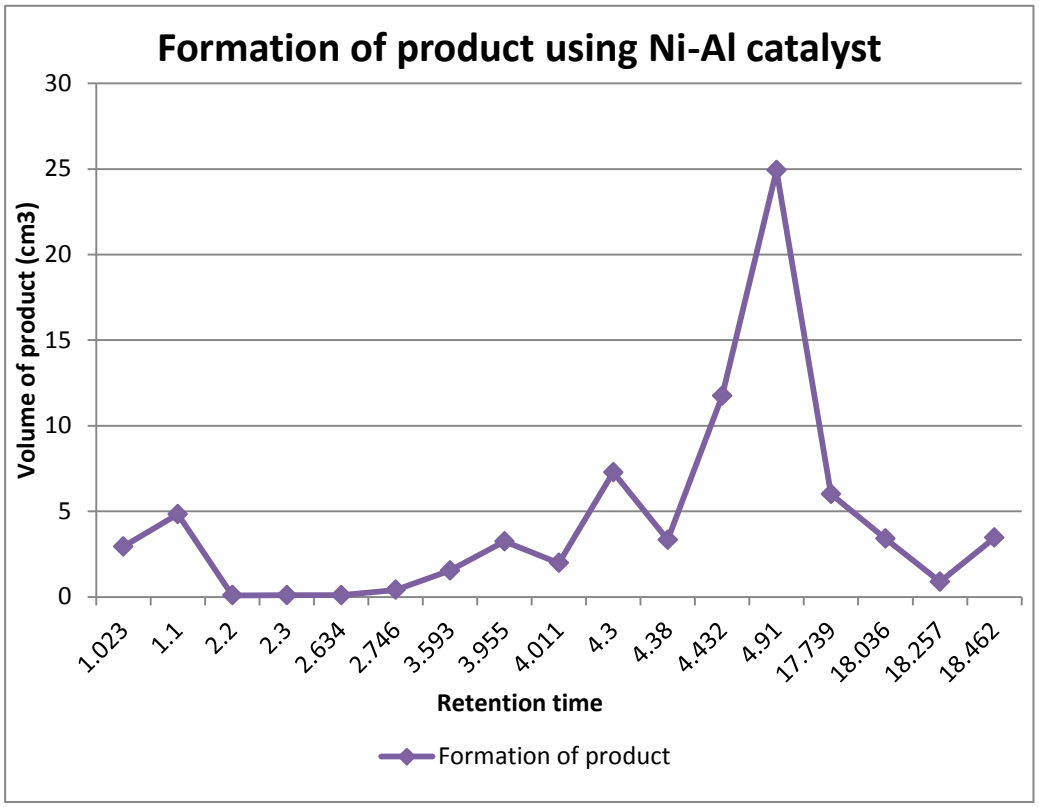


Figure 18: Graph of formation of product using Ni-Al catalyst

Referring to Figure 18, the respective components formed based on the retention time is determined. Each plot of data represents a product with respective of retention time, where the highest peak proves the largest product volume formed. The graph above shows highest peak is achieved at retention time of 4.91 followed by 4.432, 4.30, 17.739 and 1.10. With this it can be concluded, Ni-Al catalyst needs higher temperature to be activated as the retention time curve is longer. The higher temperature condition will help to excite the molecules earlier as the collision will be much more vigorous to fasten the chemical reactions (Dagle et al., 2014).

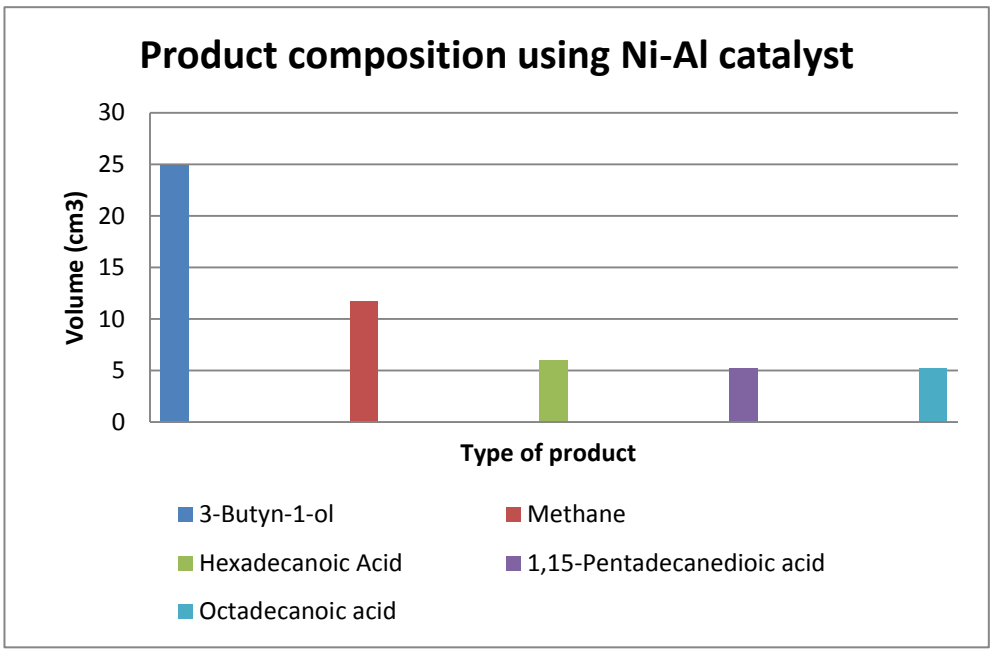


Figure 19 : Graph of product composition using Ni-Al catalyst

According to the results of the bar chart, 3-Butyn-1-ol is the component with the highest amount produced at the retention time 4.910 with volume of 24.92cm^3. It is then followed by methane at the retention time 4.432 with volume of 11.74cm^3. The third highest component comprising in this conversion with the aid of Ni-Al catalyst is also hexadecanoic acid at the retention time 4.300 with volume of 7.29cm^3. Subsequent products with their respective composition are 1,15-pentadecanedioic acid and octadecanoic acid at 5.23cm^3 and 5.18cm^3. This proves that, Ni-Al catalyst is unable to convert synthesis gas up to methanol range as it could only able to reach up to methane production. Therefore it also proves that, this catalyst is more suitable for 3-Butyn-1-ol and methane production. Higher temperature and pressure of operating condition would have managed to produce methanol as it could have excited the catalyst sample to break the carbon bond in methane to produce methanol.

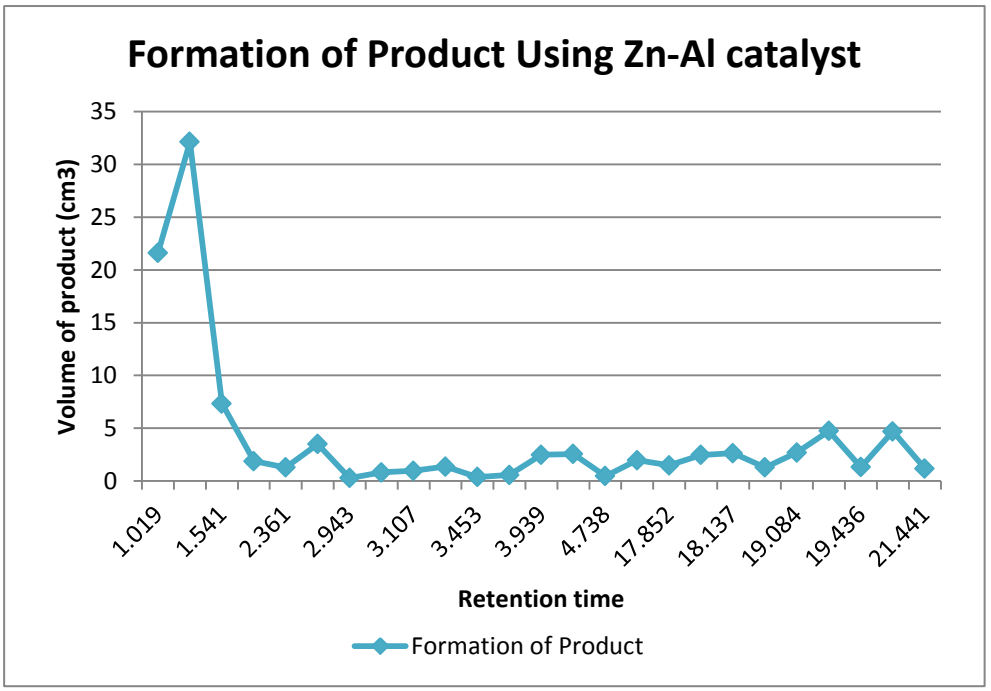


Figure 20: Graph of formation of product using Zn-Al catalyst

Referring to Figure 20, the respective components of product formation with the highest volume occurs at the retention time of 1.541 followed by 1.019l, 1.541, 19.436 and 19.084. Retention time to form products is much more shorter for Zn-Al catalyst comparable to Ni-Al catalyst where it can be deduced that the temperature used is reasonably suitable as it rapidly formed product in higher volume at a very beginning time frame but it tend to decrease rapidly in the following section. Hence, this temperature should be used in a more optimum temperature condition in order to have a constant production of products rather than a rapid in the beginning and decreased in the following period. This would affect the production rate and quality of products produced.

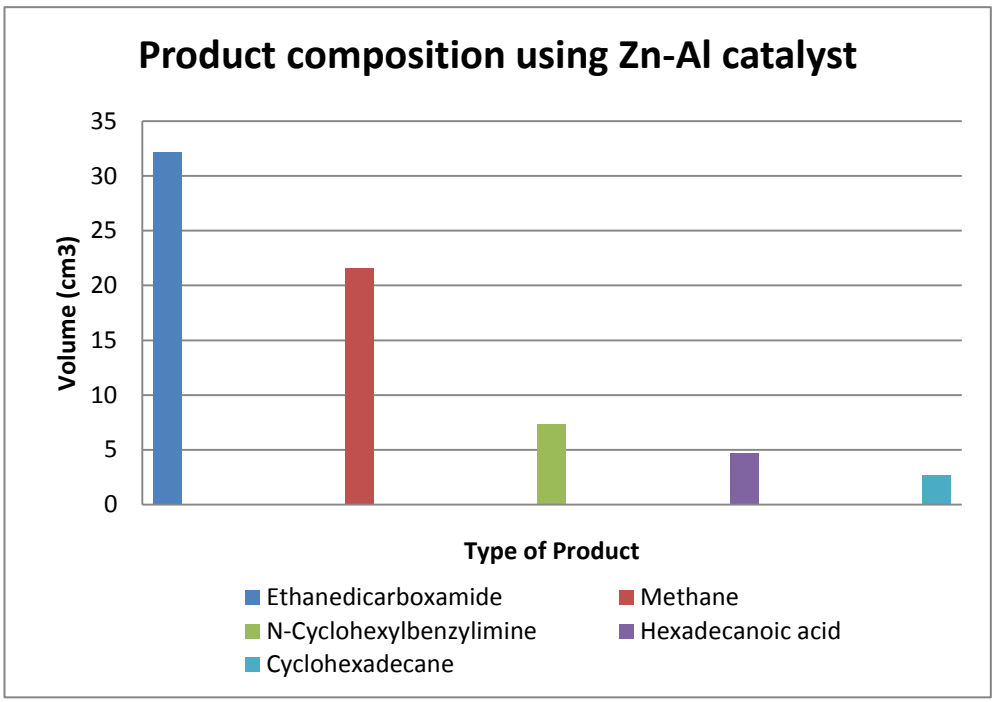


Figure 21: Graph of product composition Using Zn-Al catalyst

According to the results above, ethanedicarboxamide is the component with the highest amount produced at the retention time 1.128 with volume of 32.14cm^3. It is then followed by methane as well at the retention time 1.019 with covering area of 21.61m^3. The third highest component comprising in this conversion with the aid of Ni-Al catalyst is N-cyclohexylbenzylimine at the retention time 1.541 with covering are of 7.31cm^3. Subsequent products with their respective composition are hexadecanoic acid and cyclohexadecane acid at 4.74cm^3 and 2.70cm^3. This proves that, Zn-Al catalyst unable to convert synthesis gas up to methanol range as it could only able to reach up to methane production. Higher temperature and pressure condition would have activated higher catalytic reaction of the catalyst sample to convert the methane produced to methanol by breaking the carbon bonds. Therefore it also proves that, this catalyst is more suitable for ethanedicarboxamide and methane production.

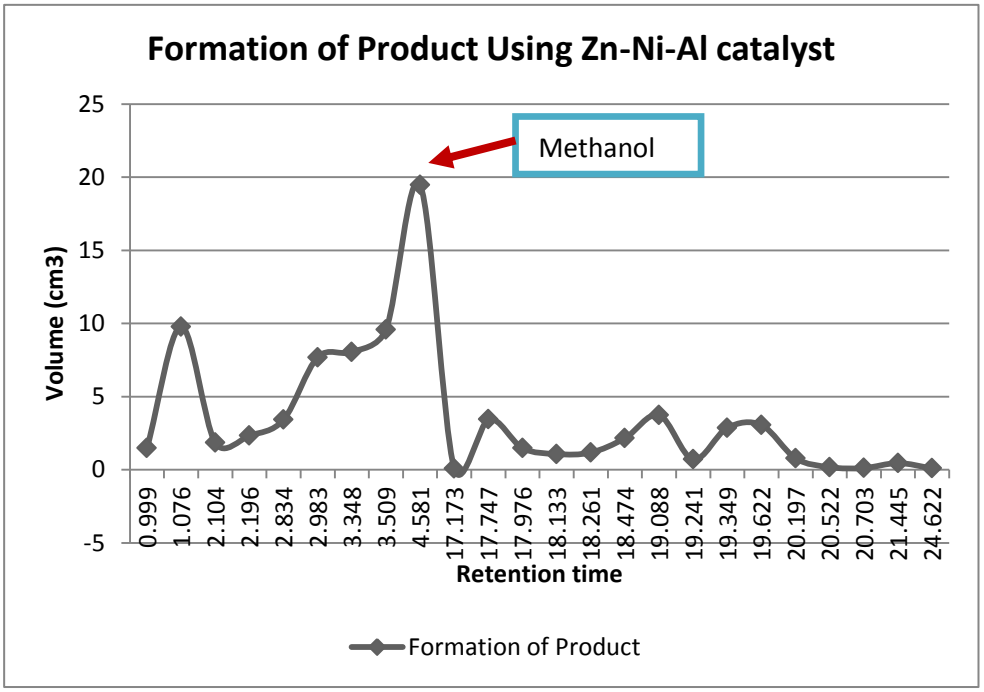


Figure 22: Graph of formation of product using Zn-Ni-Al catalyst

Referring to Figure 22, the respective components of product formation with the highest volume occurs at the retention time of 4.581 followed by 3.509, 3.348, 2.983 and 1.076. Retention time to form products is much more moderate and very suitable compared to Ni-Al and Zn-Al catalyst comparable to Ni-Al catalyst where it can be deduced that the temperature used is reasonably suitable as it rapidly formed product in higher volume at a very middle time frame. Hence, this temperature proves as optimum temperature condition in order to have a constant production of products which turned to be methanol at 4.581.

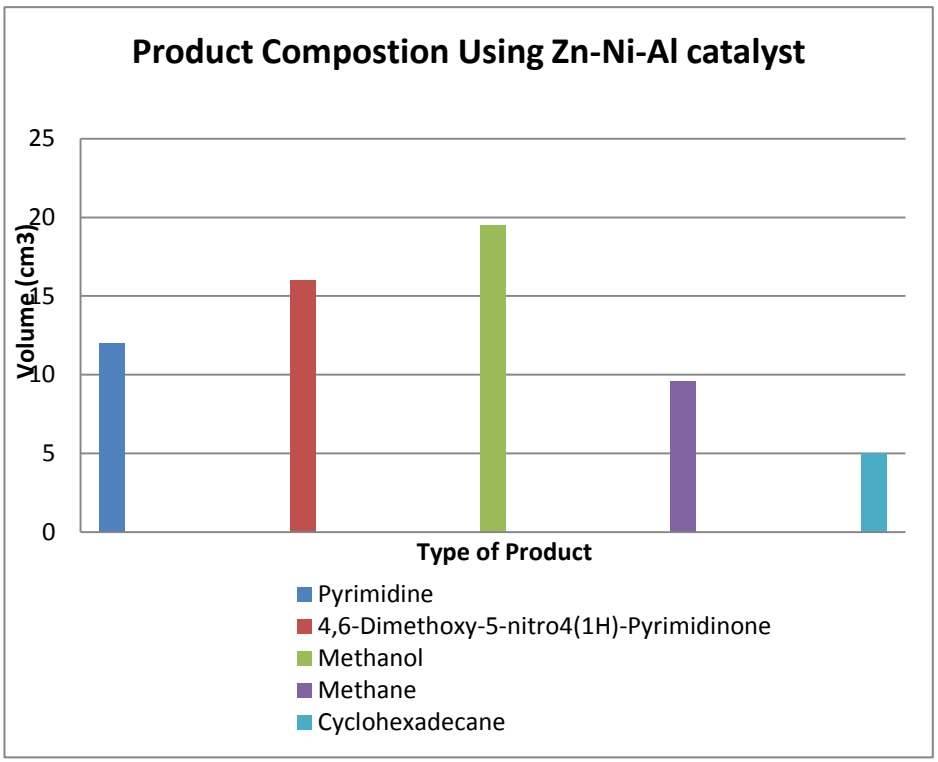


Figure 23: Graph of Product Composition Using Zn-Ni-Al

According to the results, methanol followed by 4,6-dimethoxy-5-nitro4(1H)-Pyrimidinone and pyrimidineare the 3 highest component with the highest amount produced at the retention time 4.581,3.549 and 3.308 with volume of 19.49 cm^3, 16.88cm^3 and 12.02cm^3. The following component comprising in this conversion with the aid of Zn-Ni-Al catalyst is methane at the retention time 2.983 with covering are of 9.59cm^3. Finally, cyclohexadecane is part of the product with area coverage of 5.00cm^3. Induction of higher pressure condition would have activated higher catalytic reaction of the catalyst sample to convert the methane produced to methanol by breaking the carbon bonds. Besides that, it would also boost the higher production of methanol yield as mentioned by (Liu, Murata, Inaba, & Takahara, 2013) Therefore it also proves that, this trimetallic catalyst is the most suitable for the production of synthesis gas into methanol compared to Ni-Al and Zn-Al.

Optimum Catalyst

Based on the results above, it can be concluded that Zn-Ni-Al is the most suitable catalyst comparatively to Ni-Al and Zn-Al for the conversion of synthesis gas into methanol. Among the reasons which support this statement is the presence of the combination metal catalyst in this trimetallic combination which indirectly

differentiates the structure of the catalyst that improves the overall reaction compared to bimetallic combination catalyst. It was proven as well based on the RAMAN results where the molecular vibrations differs and higher for Zn-Ni-Al catalyst compared to Ni-Al and Zn-Al catalyst The presence of both Zn and Ni in the combination metal catalyst has activated an improvised chemical reaction for the methanol production from synthesis gas. Besides that, the characterization of Zn-Ni-Al catalyst also supports these findings where it has smallest pore which produces a larger surface area for catalytic reaction to take place. Hence, this proves the main reason on the highest production of methanol yield compared to 2 other samples. Besides that, presence of Zn-Ni-Al has higher metal dispersion level and unique properties comparable when they are bimetallic.(Heracleous et al., 2013) FESEM findings also proves Zn-Ni-Al catalyst has more homogenous structure to favour the methanol production process comparable to 2 other bimetallic catalyst. The perfect combination and uniform dispersion of nickel and zinc metal based on EDX mapping proves that Zn-Ni-Al catalyst will have favourable catalytic reaction in producing highest methanol yield.

Overall these results were produced in a limitation environment where the reactor was not in the optimum condition due to some technical manufacturing defects. The reactor pressure controller was not in a good manner and it only managed to reach up to 2 bar pressure where as methanol production required 8 bar and above for an optimum result to be produced.

Hence, the recommendation to improve this overall project would be using a reactor at its best condition with proper pressure and temperature without any obstacles. Setting up pressure at 8 bar and above can produce a higher content of methanol as higher pressure would enable the catalyst to be in a better optimum condition to support the overall operating condition for a higher conversion. Besides that, using trimetallic combination catalyst would produce higher volume of methanol compared using bimetallic catalyst as it will be able break the methane bond to form methanol.

CHAPTER 5 CONCLUSION AND RECOMMENDATION

This chapter discusses about the conclusions of the overall project including the recommendation for future study. This will be essential as it can improve the overall progress of this study for future research.

The main aim of this project is to fulfill the 3 main aspects which is stated below:

a) To determine the catalyst synthesis of hydrotalcite derived catalyst compound via co-precipitation method.
b) To evaluate the catalyst characterization of the catalyst.
c) To determine the conversion rate of syngas into methanol by all the catalyst and choose the optimum hydrotalcite derived catalyst based on the findings.

Based on the aims and objective of the project, the (a), (b) and (c)objectives have been successfully achieved. For objective (a), co-precipitation method have been used in order to produce hydrotalcite derived catalyst. Besides that, for objective (b), RAMAN Spectroscopy, BET and FESEM characterization test has been conducted for the catalyst sample to study the molecular vibration and topographical structure of the respective catalyst. For objective (c), the 3 catalyst samples have been tested with hydrocarbon cracking reactor with the presence of CO, $H_2$and N_2 to collect the product gas. Following that, GCMS test have been conducted to determine amount of methanol produced from the respective product of catalyst samples. Based on the results obtained from the overall project, Zn-Ni-Al is the most suitable hydrotalcite derived catalyst which supports the conversion of synthesis gas into methanol compared to Ni-Al and Zn-Al catalyst where it had produced the highest amount methanol yield of 19.49 cm^3.

The recommendation of the project will be in terms of typesof transition metals used for the catalyst synthesis. It is very much encouraged for future study to implement trimetallic catalyst compared to bimetallic catalyst based to be tested for the production of methanol based on the results obtained from this project. Besides that, maintaining the condition of equipments in highest level. Among those is the hydrocarbon cracking reactor and FESEM machine.

Frequent breakdown of these equipments have caused major impact in delay for the progress of the overall project. Besides that, the pressure controller of the reactor also needed to be regularly undergoing maintenance as it will help to preserve the conditions at the optimum level since pressure plays a major role in synthesis gas conversion into methanol.

Overall this project is very much compatible and feasible to be completed in the duration of 28 weeks with the supervision of a Chemical Engineering lecturer. Hence this study is very much welcomed to be continued with various type of hydrotalcite derived catalyst in order to improve the methanol production yield at a lower pressure and temperature.

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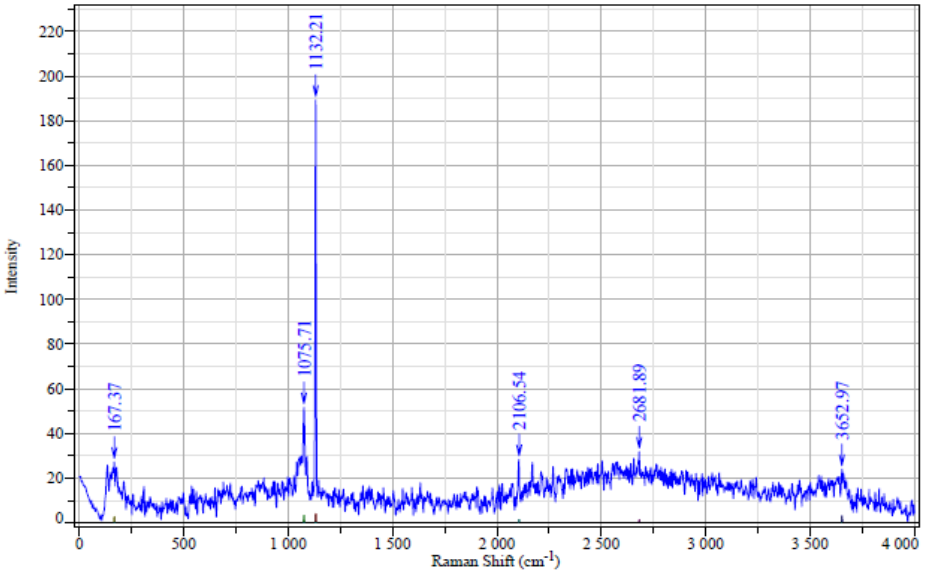
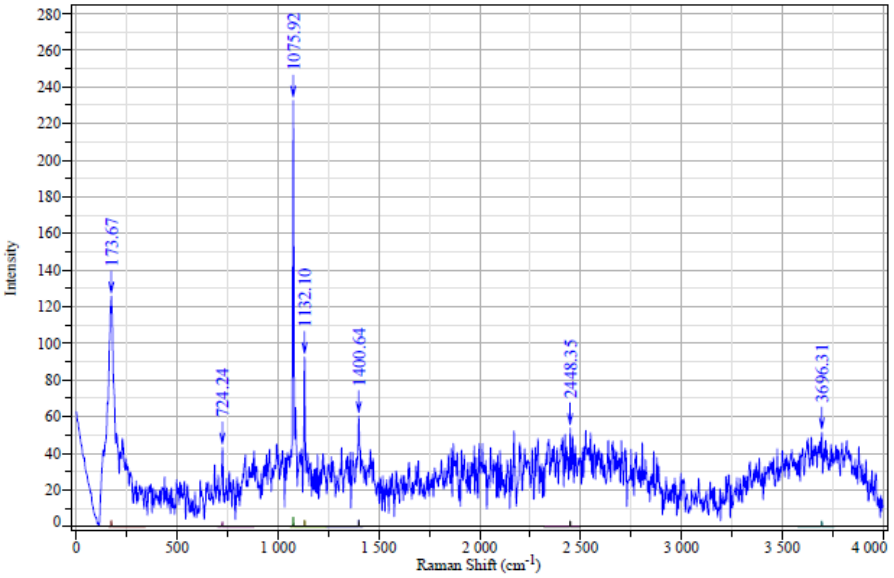
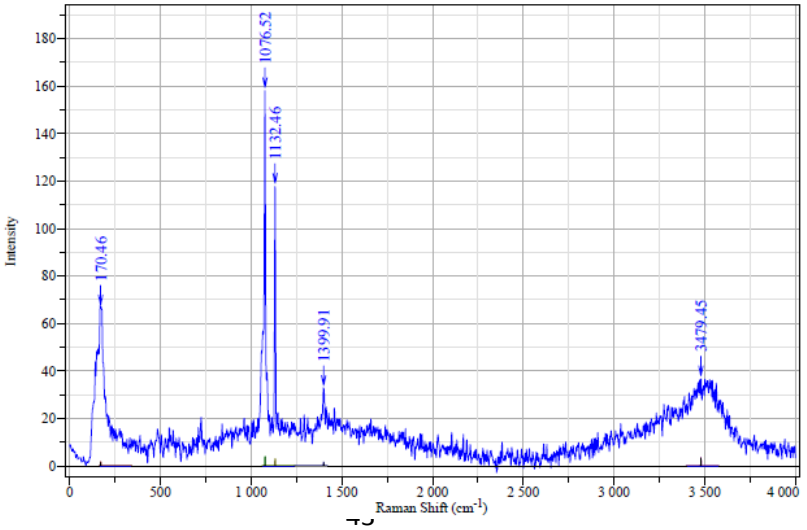
APPENDICES

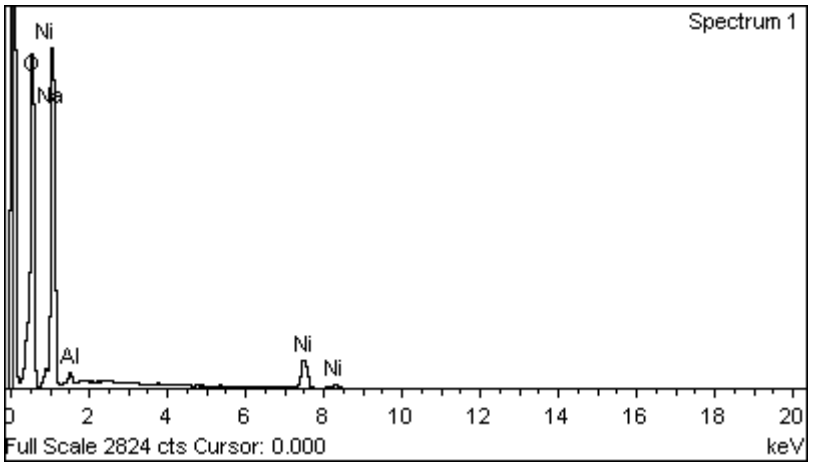
APPENDIX I :RAMAN Raw data (Ni-Al,Zn-Al-Zn-Ni-Al)

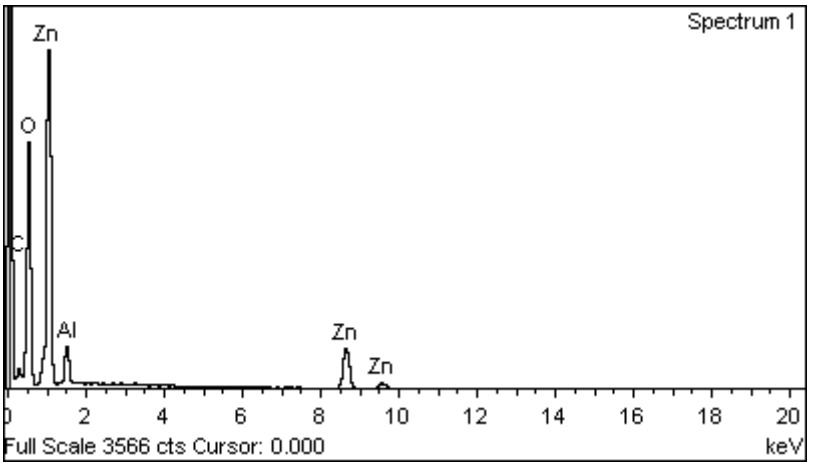


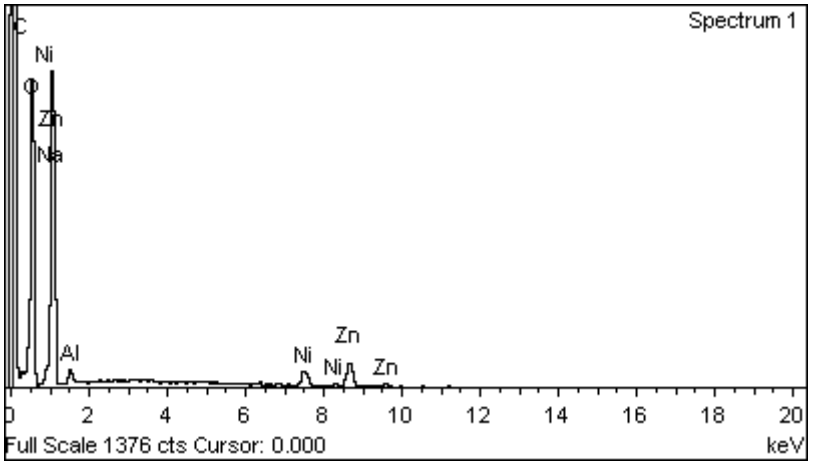




APPENDIX II: EDX Mapping Images (Ni-Al, Zn-Al, Zn-Ni-Al)







APPENDIX III : GCMS DATA